



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT TRANSMITTAL

Patent No.: 6,727,377
Issued: April 27, 2004
Name of Patentee: The Penn State Research Foundation
Title of Invention: ASYMMETRIC CATALYSIS BASED ON CHIRAL
PHOSPHOLANES AND HYDROXYL PHOSPHOLANES
Customer No.: 27,623
Attorney Docket No.: 823.0090USQ

Certificate
JUN 29 2004
of Correction

Mail Stop Certificate of Correction Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

We are enclosing:

1. Request for Certificate of Correction of Patent for PTO Mistake under 37 CFR 1.322(a);
2. Copy of an Amendment, filed on October 17, 2003;
3. PTO Form 1050 in duplicate;
4. Transmittal Letter in duplicate; and
5. Postcard.

Please charge any additional fees or credit any such fees, if necessary to Deposit Account No. 01-0467 in the name of Ohlandt, Greeley, Ruggiero & Perle. A duplicate copy of this sheet is attached.

Respectfully submitted,

Date: June 22, 2004

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CERTIFICATE OF MAILING

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE U.S. POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO: MAIL STOP: CERTIFICATE OF CORRECTION BRANCH, COMMISSIONER FOR PATENTS, P.O. BOX 1450, ALEXANDRIA, VA 22313-1450 ON June 22, 2004.

Leslie Moscatello
NAME

SIGNATURE

6/22/04
DATE

29 JUN 2004

UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO.: 6,727,377

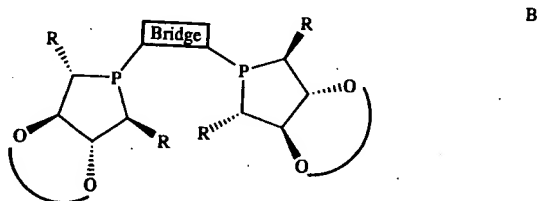
DATED: April 27, 2004

INVENTORS: Xumu Zhang

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 28

Claim 1, in formula B' structure, phosphorous containing five-member ring on the left side of the bridge, going clockwise from phosphorous atom, the first R is up (solid line), the first O is down (dotted line), the second O should be up (solid line) instead of down (dotted line) as it appears in the patent, the second R is down (dotted line).



Column 30

Line 12, Claim 7, should read: "A catalyst according to claim 6 wherein the transition metal is Rh."

Column 30

Line 61, Claim 10, "C)" should read --CO--

Line 62, "where R⁹ C₁-C₈" should read --where R⁹ is C₁-C₈--

MAILING ADDRESS OF SENDER:

Patent No.: 6,727,377

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29 JUN 2004

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: X. Zhang
Serial No: 09/992,551
Filed: November 6, 2001
Title: Asymmetric Catalysis Based on Chiral Phospholanes and Hydroxyl Phospholanes

Docket No.: 823.0090USQ
Examiner: Taofiq A. Solola
Art Unit: 1626
Confirmation No.: 1453
Customer No.: 27623

Mail Stop: AF

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

AMENDMENT AFTER FINAL

In response to the Office Action mailed on July 2, 2003, please amend this application as follows:

IN THE CLAIMS:

Please cancel claims 31-34.

Please add the newly presented claims 43-46.

Please amend the claims as follows:

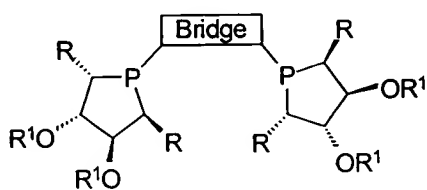
Amendments to the Claims

This listing will replace all prior versions and listings of claims in the application:

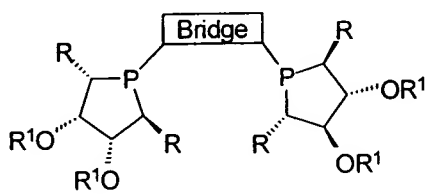
Listing of Claims

Claims 1-22 (withdrawn)

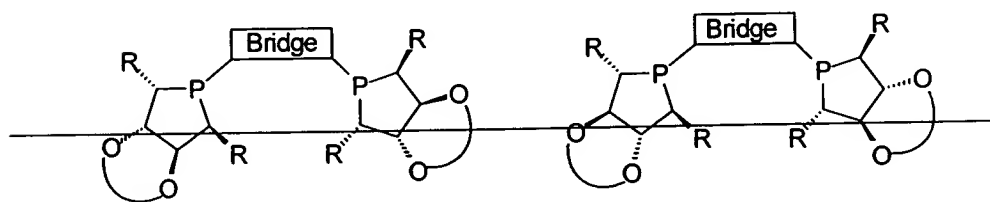
Claim 23. (currently amended) A catalyst comprising a chiral compound in the form of a complex with a transition metal wherein said compound is selected from compounds represented by the formula B, B', D, D' or the corresponding enantiomers:



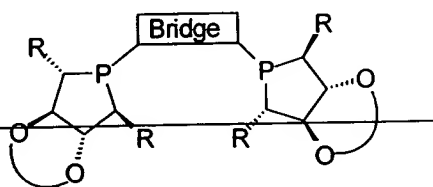
A



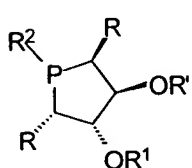
A'



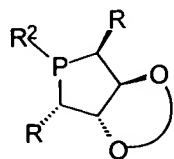
B



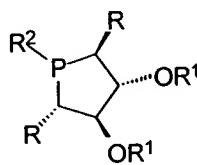
B'



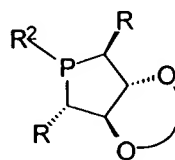
C



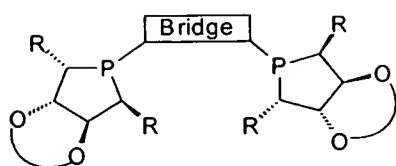
D



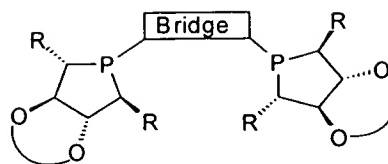
C'



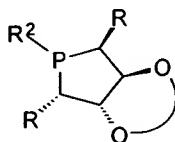
D'



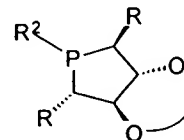
B



B'




D



D'

wherein:

- a) R and R² are independently aryl, alkyl, alkyl aryl, aryl alkyl, or chiral oxazolino which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol or dialkylamino groups;
- b) ~~R¹ can be H, alkyl, silane, aryl, a water soluble unit, or a linked polymer chain or inorganic support; and the ring component~~  ~~O represents a protected diol, a crown ether linkage, -O-alkyl-O- wherein the alkyl group is linked to a polymer, or -O-(CH₂CH₂-O)_n- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by C1-C8 alkyl;~~

- c) in formulas B and B', the Bridge may be:

$-(CH_2)_n-$ where n is an integer ranging from 1 to 8;

$-(CH_2)_nX(CH_2)_m-$ wherein n and m are each integers, the same or different, ranging from 1 to 8, and X is O, S, NR^4 , PR^4 , AsR^4 , SbR^4 , divalent aryl, divalent fused aryl, divalent 5-membered ring heterocyclic group, or divalent fused heterocyclic group, wherein R^4 is aryl, alkyl, substituted aryl, or substituted alkyl; or

1,2-divalent phenyl, 2,2'-divalent 1,1'-biphenyl or 2,2'-divalent 1,2'-binaphthyl or ferrocene, each of which may be substituted with aryl, C1-C8 alkyl, F, Cl, Br, I, $COOR^5$, SO_3R^5 , $PO_3R^5_2$, OR^5 , SR^5 , NR^5_2 , PR^5_2 , AsR^5_2 , or SbR^5_2 ;

wherein the substitution on 1,2-divalent phenyl, the ferrocene or biaryl bridge can be independently halogen, alkyl, alkoxyl, aryl, aryloxy, nitro, amino, vinyl, substituted vinyl, alkynyl, or sulfonic acids; and

R^5 is hydrogen, C1-C8 alkyl, C1-C8 fluoroalkyl, or C1-C8 perfluoroalkyl, aryl; substituted aryl; arylalkyl; ring-substituted arylalkyl; or $-CR^3_2(CR^3_2)_qX(CR^3_2)_pR^1$ wherein q and p are integers, the same or different, ranging from 1 to 8; R^3 is aryl, alkyl, substituted aryl, or substituted alkyl; and X is as defined above.

Claim 24. (original) A catalyst according to claim 23, wherein the transition metal is rhodium, iridium, ruthenium, nickel, or palladium.

Claim 25. (currently amended) A catalyst according to claim 24, wherein said transition metal complex is formed from a compound ~~is a complex with a compound~~ selected from the group consisting of: $Pd_2(DBA)_3$, $Pd(OAc)_2$, $[Rh(COD)Cl]_2$, $[Rh(COD)_2]X$, $Rh(acac)(CO)_2$, $RuCl_2(COD)$, $Ru(COD)(methylallyl)_2$, $Ru(Ar)Cl_2$, wherein Ar is an aryl group, unsubstituted or substituted with an alkyl group; $[Ir(COD)Cl]_2$, $[Ir(COD)_2]X$; and $Ni(allyl)X$; wherein X is a counterion.

Claim 26. (original) A catalyst according to claim 25, wherein X is selected from the group consisting of: F^- , Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , SbF_6^- , $CF_3SO_3^-$, and PF_6^- .

Claim 27. (original) A catalyst according to claim 26 wherein X is PF_6^- .

Claim 28. (original) A catalyst according to claim 24 wherein the transition metal is Ru or Rh.

Claim 29. (original) A catalyst according to claim 28 wherein the transition metal is Rh.

Claim 30. (currently amended) A catalyst according to claim 23, wherein said transition metal complex is formed from a compound selected from the group consisting of: the catalyst comprises: Ru(RCOO)₂(diphosphine), RuX₂(diphosphine), Ru(methylallyl)₂(diphosphine), Ru(aryl group)X₂(diphosphine), Rh(RCOO)₂(diphosphine), RhX₂(diphosphine), Rh(methylallyl)₂ diphosphine, or Rh(aryl group)X₂ (diphosphine) and X is halogen.

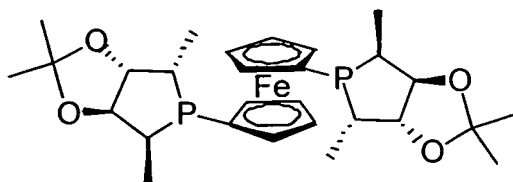
Claim 31. (canceled)

Claim 32. (canceled)

Claim 33. (canceled).

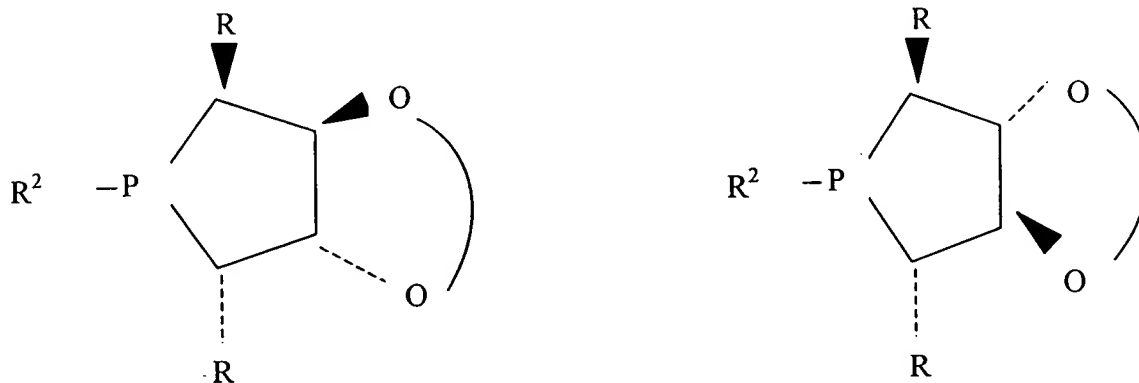
Claim 34. (canceled)

Claim 35. (Previously presented) A catalyst according to claim 23, wherein said chiral compound is represented by the following formula:



24 f-ketalPhos

Claim 36. (currently amended) A catalyst according to claim 23 comprising a transition metal complex of a compound of the following formula or its enantiomer:



wherein

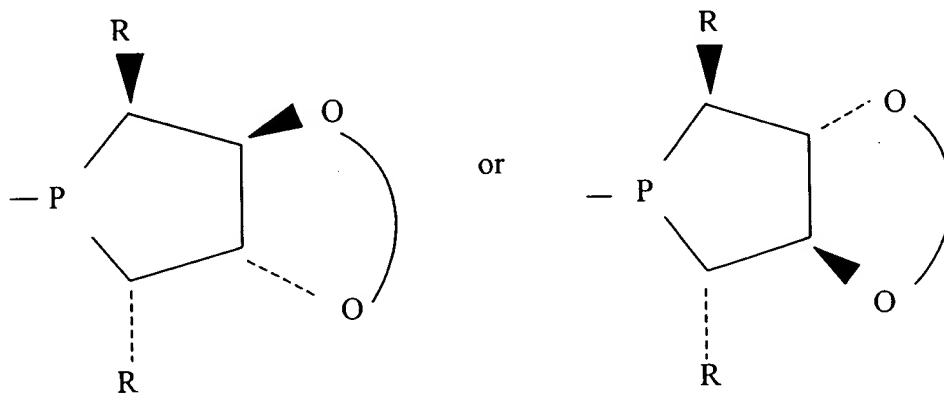
- A) R is C₁-C₈ alkyl, C₁-C₈ alkyl aryl, aryl C₁-C₈ alkyl, aryl, each of which may be substituted with carboxylic acid, alkoxy, hydroxy, alkylthio, thiol, dialkylamino, diphenylphosphino or chiral oxazoline; and
- B) the ring component $\text{O} \cdots \text{O}$ represents a protected diol, a crown ether linkage, -O-C₁-C₈ alkyl-O- wherein the alkyl group is linked to a polymer, -O-(CH₂CH₂)_n-O- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by C₁-C₈ alkyl, or O-W-O, where W is BR⁹, POR⁹, PO(OR⁹), SO₂, CO, or Si(R⁹)₂; where R⁹ is C₁-C₈ alkyl, aryl, C₁-C₈ alkyl aryl, or aryl C₁-C₈ alkyl, alkoxy, hydroxy, alkylthio, thio, alkylamino, dialkylamino; and
- C) R² is either R, H, phenyl or a symmetrical bidentate structure having the formula



wherein BRIDGE is

- i) $-(CH_2)_n-$ where n is an integer from 1 to 8; or
- ii) $-(CH_2)_n X (CH_2)_m-$ where n and m are the same or different integers from 1 to 8, and X is O, S, NR^4 , PR^4 , AsR^4 , SbR^4 , divalent aryl, divalent fused aryl, divalent 5-membered heterocyclic ring, or divalent fused heterocyclic ring, where R^4 is C^1 - C^8 alkyl, aryl, substituted aryl, or substituted alkyl; or
- iii) 1, 2-divalent phenyl, 2, 2'-divalent 1, 1'-biphenyl, 2,2'-divalent, 1,1' binaphthyl, or ferrocene, each of which may be substituted independently with $C_1 - C_8$ alkyl or aryl, F, Cl, Br, I, $COOR^5$, SO_3R^5 , $PO_3R^5_2$, OR^5 , SR^5 , NR^5_2 , PR^5_2 , AsR^5_2 , SbR^5_2 , nitro, vinyl, substituted vinyl, alkynyl wherein R^5 is H, C_1 - C_8 alkyl, substituted C_1 - C_8 alkyl, C_1 - C_8 fluoroalkyl, C_1 - C_8 perfluoroalkyl, aryl or substituted aryl; and

wherein Z is a compound selected from the group of compounds having the following formulas and their corresponding enantiomers:



Claims 37-42 (withdrawn)

Claim 43. (new) A catalyst according to claim 36, wherein the transition metal is rhodium, iridium, ruthenium, nickel, or palladium.

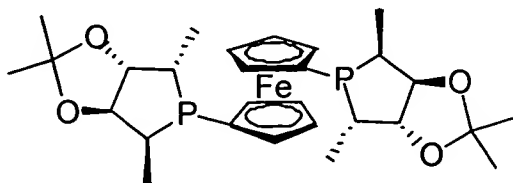
Claim 44. (new) A catalyst according to claim 36, wherein said transition metal complex is formed from a compound selected from the group consisting of:

$\text{Pd}_2(\text{DBA})_3$, $\text{Pd}(\text{OAc})_2$; $[\text{Rh}(\text{COD})\text{Cl}]_2$, $[\text{Rh}(\text{COD})_2]\text{X}$, $\text{Rh}(\text{acac})(\text{CO})_2$; $\text{RuCl}_2(\text{COD})$, $\text{Ru}(\text{COD})(\text{methylallyl})_2$, $\text{Ru}(\text{Ar})\text{Cl}_2$, wherein Ar is an aryl group, unsubstituted or substituted with an alkyl group; $[\text{Ir}(\text{COD})\text{Cl}]_2$, $[\text{Ir}(\text{COD})_2]\text{X}$; and $\text{Ni}(\text{allyl})\text{X}$; wherein X is a counterion selected from the group consisting of: F^- , Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , SbF_6^- , CF_3SO_3^- , and PF_6^- .

Claim 45. (new) A catalyst according to claim 36, wherein said transition metal complex is formed from a compound selected from the group consisting of:

$\text{Ru}(\text{RCOO})_2(\text{diphosphine})$, $\text{RuX}_2(\text{diphosphine})$, $\text{Ru}(\text{methylallyl})_2(\text{diphosphine})$, $\text{Ru}(\text{aryl group})\text{X}_2(\text{diphosphine})$, $\text{Rh}(\text{RCOO})_2(\text{diphosphine})$, $\text{RhX}_2(\text{diphosphine})$, $\text{Rh}(\text{methylallyl})_2 \text{ diphosphine}$, or $\text{Rh}(\text{aryl group})\text{X}_2 (\text{diphosphine})$ and X is halogen.

Claim 46. (new) A catalyst according to claim 36, wherein said compound is represented by the following formula:



24 f-ketalPhos

wherein said transition metal is rhodium, iridium, ruthenium, nickel or palladium;
 and wherein said transition metal complex is formed from: $\text{Pd}_2(\text{DBA})_3$, $\text{Pd}(\text{OAc})_2$;
 $[\text{Rh}(\text{COD})\text{Cl}]_2$, $[\text{Rh}(\text{COD})_2]\text{X}$, $\text{Rh}(\text{acac})(\text{CO})_2$; $\text{RuCl}_2(\text{COD})$, $\text{Ru}(\text{COD})(\text{methylallyl})_2$,
 $\text{Ru}(\text{Ar})\text{Cl}_2$ wherein Ar is an aryl group unsubstituted or substituted with an alkyl group,
 $[\text{Ir}(\text{COD})\text{Cl}]_2$, $[\text{Ir}(\text{COD})_2]\text{X}$ or $\text{Ni}(\text{allyl})\text{X}$, wherein X is a counterion selected from the group
 consisting of: F^- , Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , SbF_6^- , CF_3SO_3^- , and PF_6^- ; or
 $\text{Ru}(\text{RCOO})_2(\text{diphosphine})$, $\text{RuX}_2(\text{diphosphine})$, $\text{Ru}(\text{methylallyl})_2(\text{diphosphine})$, $\text{Ru}(\text{aryl}$
 $\text{group})\text{X}_2(\text{diphosphine})$, $\text{Rh}(\text{RCOO})_2(\text{diphosphine})$, $\text{RhX}_2(\text{diphosphine})$, $\text{Rh}(\text{methylallyl})_2$
 diphosphine or $\text{Rh}(\text{aryl group})\text{X}_2(\text{diphosphine})$, wherein X is halogen.

REMARKS

Claims 31-34 have been canceled. Therefore, their rejection is moot.

New claims 43-46 have been added.

Applicant gratefully acknowledges the allowance of claim 35 and the allowability of claims 36 if written in independent form.

Applicant has written claim 36 in independent form. Therefore claim 36 should be allowed.

Regarding the allowed claim 35, which depends from claim 23, the Office Action did not indicate that claim 35 should also be written in independent form, even though claim 35 depended from a rejected base claim. Accordingly, the applicant did not amend the allowed claim 35. Although the Applicant anticipates that base claim 23, as amended, will now be allowable, applicant reserves the right to rewrite claim 35 in independent form to preserve the allowance of claim 35 in the event that claim 23 were to remain rejected. Therefore, the Applicant would appreciate a telephone call from the Examiner so that claim 35 could be amended by an Examiner's Amendment to place it in independent form.

Applicant has amended claim 23 to delete formulas A, A', C and C' and to define that the ring component $\text{O} \begin{array}{c} \text{---} \end{array} \text{O}$ in B, B', D and D' represents "a protected diol, a crown ether linkage, -O-alkyl-O- wherein the alkyl group is linked to a polymer, or -O-(CH₂CH₂-O)_n- wherein n is an integer ranging from 1 to 8 and the methylene groups are optionally substituted by C1-C8 alkyl;". Support for this amendment is in claim 36 and the specification.

Applicant has amended claims 25 and 30 to define that transition metal complex is formed from the compounds shown (i.e., ligands).

Claims 23-34 have been rejected under 35 U.S.C. § 102(b) as being anticipated by Drent et al. (EP 0 501 586 A2).

Applicant respectfully points out that the ligands represented by the formulas shown in the claimed catalyst defined by claim 23 do not have "a phosphorus bidentate ligand of the general formula $R^1R^2P-R-PR^3R^4$ in which R^1 to R^4 represent identical or different optionally polar substituted aromatic hydrocarbyl groups and R represents a divalent bridging group containing at least two carbon atoms in the bridge linking the two phosphorus atom."

Compounds having the "formula $R^1R^2P-R-PR^3R^4$ in which R^1 to R^4 represent identical or different optionally polar substituted aromatic hydrocarbyl groups..." are not chiral due to the **free rotation around each of the P-R bonds** in the $R^1R^2P-R-PR^3R^4$ structure. As the Applicant stated in the previous Response to Office Action, none of the compounds described Drent et al. are chiral. There is no chirality in $R^1R^2P-R-PR^3R^4$ because they are identical or different **aromatic hydrocarbyl groups**. To exhibit chirality in such systems, either the bridge or at least two of the R^1 , R^2 , R^3 or R^4 together must be part of a rigid structure.

Further, none of the examples mention any chiral phosphorus bidentate ligands. Applicant respectfully requests the if there are such examples, their location should be pointed out by the Examiner.

Even if the compounds described Drent et al. were chiral, still the instantly claimed catalysts having ligands represented by formulas B, B', D, D' or their enantiomers are neither taught nor suggested by the disclosure of Drent et al.

The ligand in the instantly claimed catalyst has two rigid 5-membered phospholane rings and each of the phospholane rings is further fused with a rigid 5-membered ketal ring. None of the compounds described Drent et al. have "two rigid 5-membered phospholane rings and each of the phospholane rings is further fused with a rigid 5-membered ketal ring." Such ligands are neither taught nor suggested in the disclosure of Drent et al. Applicant respectfully requests that if there are such examples, their location should be pointed out by the Examiner. Without such a showing, the instantly claimed catalyst would not be anticipated by Drent et al.

Accordingly, claim 23 and claims 24-30, which depend directly or indirectly from claim 23, are allowable Drent et al.

Claims 23-34 have been rejected under 35 U.S.C. § 102(e) as being anticipated by Sturmer et al. (U.S. Patent No. 6, 043,396).

The Examiner has stated that Sturmer et al. "embrace the instant compounds A and C...". Applicant has deleted compounds A, A', C and C' from claim 23. Applicant has further canceled claims 31-34 which are directed to compounds A, A', C or C'. Thus, the Sturmer et al. patent does not disclose or suggest the catalysts defined by claim 23, as amended.

Accordingly, claims 23 and 24-30, which depend directly or indirectly from claim 23, are allowable.

Claims 23-34 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Brunner et al. publication in Zeitschrift fur Naturforschung.

Compounds described by Brunner et al. publication correspond to compounds represented by the formulas: A, A', C or C'. Applicant has deleted compounds A, A', C and C' from claim 23. Applicant has further canceled claims 31-34 which are directed to compounds represented by the formulas A, A', C or C'. Thus, the Brunner et al.

publication in Zeitschrift fur Naturforschung does not disclose or suggest the catalysts defined by claim 23, as amended.

Therefore, claims 23 and 24-30, which depend directly or indirectly from claim 23, are allowable.


In view of the foregoing, claim 23 and claims 24-30, which depend directly or indirectly from claim 23, as well as the newly presented claims 43-46 are allowable.

Accordingly, the Applicant respectfully requests reconsideration and allowance of all pending claims.

Respectfully submitted,

Date: October 2, 2003

By:



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